# The production of single crystals of lithium fluoride

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# THE PRODUCTION OF SINGLE CRYSTALS OF LITHIUM FLUORIDE.

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## Iotroduction.

It is well known that crystalline lithium fluoride transmits further into ultraviolet than any other known substance and as clearly as fluorite in the region of $1\sim6\,\mu$ wave length of infrared and is water-proof better than rock-salt or sylvine and is applied extensively to spectrum analysis. As there is no appearance of lithium fluoride in nature, a number of investigators[1-4] prepared the compound and crystallized it from the melt in the laboratory. D. C. Stockbarger[5] prepared lithium fluoride from lithium carbonate and fluoric acid and crystallized it by the modification of the P. W. Bridgman[6] method of lowering a pointed bottom crucible along the axis of a vertical tubular furnace and prepared crystalline lithium fluoride of 3 inches in diameter.

The authors prepared lithium fluoride by the double decomposition between lithium chloride and ammonium fluoride and transparent, colourless single crystals smaller by about 2 cm in diameter, 1 cm in height than the platinum vessel from the salt by repeating the modification of the von S. Kyropoulos[2] scheme in which the large single crystal grown from a seed in a melt is slowly raised. Some of the physical properties of the crystal obtained in their laboratory are tested.

## Preparation of lithium fluoride.

It is the most important aim of this experiment to prepare economically lithium fluoride as pure as possible from chemicals, for example lithium chloride and ammonium fluoride made in Japan. The water solution of lithium chloride is acidified with hydrochloric acid and neutralized with ammoniac. The clear solution through these steps is warmed[7] and reacted by pouring the saturated water

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5) D. C. Stocklarger, *Rev. Sci. Inst.*, 7. 133 (1936)
6) P. W. Bridgman, *Proc. Am. Acad.*, 60, 305 (1925)
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solution of equivalent ammonium fluoride in a plastic vessel with violent stirring. The precipitate of lithium fluoride is separated from comparably soluble fluoride of the impurities with a plastic filter and washed several times with warm water and finally dried on a plastic plate. The yield is about 75~80 %.

## Crystallization method.

Lithium fluoride prepared above described is heated at a temperature slightly above the melting point (842°C) in a platinum vessel of 10 cm diameter and 7 cm height and cooled slowly for about 24 hours. The melted salt is opaque as a whole, but a gathering of transparent, small single crystals. One of them is set on a chrome-steel holder with a water cooler as a seed and dipped in the melt which is kept about 950°C at the surface and the growing rate is~0.5 cm in diameter per hour. The crystal grown till the permitted diameter of the platinum vessel is raised gradually at the rate of~0.5 cm in height per hour.

The growing rate of the crystallization is dependent on a certain degree of purity of the salt. It may be necessary to make the rate slow or repeat the crystallization above described, in the case of the growing crystal tends to be opaque.

## Clarity and strains.

The crystal can be cut in a cubic along cleavage as shown in photograph No. 1. Photograph No. 2 shows the crystal of~7 cm diameter (1), cut in two along cleavage (2) and polished surfaces of cleavage (3). The crystals prepared have, of course, the cylindrical shape, not the geometrical form characteristic of the crystalline system.

Light scattering of the crystal results mainly from the impurities of chemicals, dust from the surrounding in each step and hydrolysis of lithium fluoride and faulty growing conditions. The crystal is classified into three kinds by the internal light scattering. (a) Scattering is not seen. (b) The centres of scattering are disseminated in the colloidal state. (c) The centres of scattering are large and disseminated sparsely. The appearance of the cases of (b) and (c) is seen lightly coloured in the daylight. When the growing rate is too quick, or the melt is at too high temperature, the crystal such as (b) or (c) is obtained, although the salt of the same purity is used. These crystals return to the crystallization course at the specified conditions.

The internal strains of the crystal annealed for about 12 hours are not seen entirely.

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Photograph No. 1

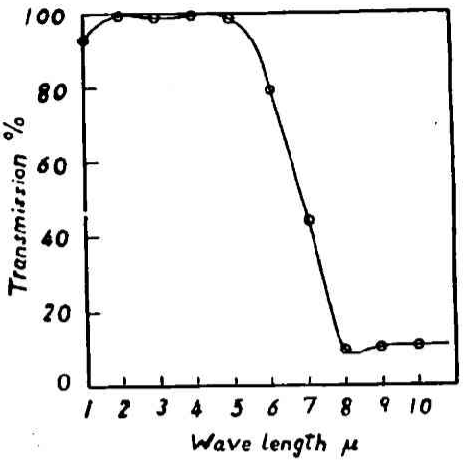
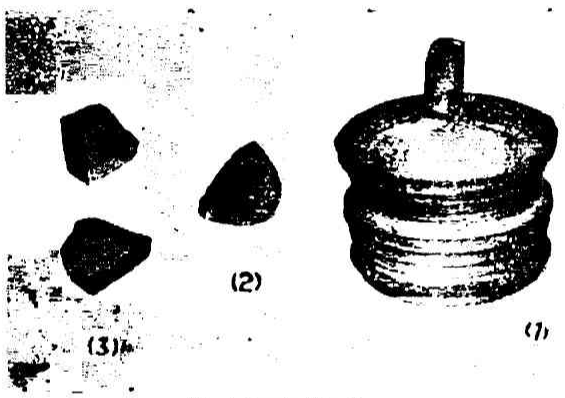



Fig. 1




Photograph No. 2

## Light transmission.

Infrared, visible and ultraviolet transmissions of several colourless crystals are observed. Infrared transmission characteristics of six samples of various thickness 4～13 mm are determined as follows, nearly 90, 100, 80, 50, 10 % transmitions for the wave lengthes 1, 2～5, 6, 7, 10 $\mu$ respectively. Fig. 1 shows infrared transmission of the crystal of a thickness 13 mm.

Colour is not visually detectable even through a thickness of 5 cm. Ultraviolet transmission of the crystal of a thickness 13 mm is tested till 180 m$\mu$ with the quartz spectrograph and the light source of the hydrogen discharge tube of Hilger type, and the same as the crystalline quartz of a thickness 10 mm.

## Consideration.

The follwing matters must be taken care to produce an excellent crystal by growing a seed from a melt.

(1) The high grade of purity of a melt is desired as possible. The melt may be purified in the course of the preparation and recrystallization.

(2) The isothermal surface considered in a melt is nearly hemispherical.

(3) The orientation of a crystal is made easy by raising the temperature of

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a melt or lowering its viscosity.

(4) Let a crystal grow from only a seed of a single crystal.

(5) The temperature difference between a seed and a melt is over the definite value. That is, the growing rate is below the definite value.

(6) The volume of a melt decreases at the crystallization, therefore, the rash growing rate of the crystallization generates the growth of small vacant spaces in a crystal.

Photograph No. 3

Photograph No. 3 shows the fact distinguished clearly between the part of the single crystal grown from a seed and the radially cracked part grown from the edge of the holder of the seed. The two parts disagree with the temperature distribution, or the growing rate.

(7) A furnace must be housed nearly completely to separate air from a melt and sealed from evolved gases.

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